Polymers from Hexafluoropropylene Oxide (HFPO)

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ABSTRACT

Mechanistic and kinetic studies of the polymerization of
hexafluoropropylene oxide (HFPO) initiated by mono-
functional and difunctional liquid catalysts have led to a
working understanding of the processes involved. Careful
control of reaction conditions with perfluorinated cesium
alkoxide initiators and perfluorinated olefin diluents per-
mits the synthesis of cleanly difunctional poly-HFPO.
These polymers undergo a wide variety of chemical re-
actions at the acyl fluoride end groups and lead to chain
extended and cross-linked high polymers with outstanding
thermal and chemical resistance.

INTRODUCTION

The epoxide ring of hexafluoropropylene oxide [1] (HFPO) readily
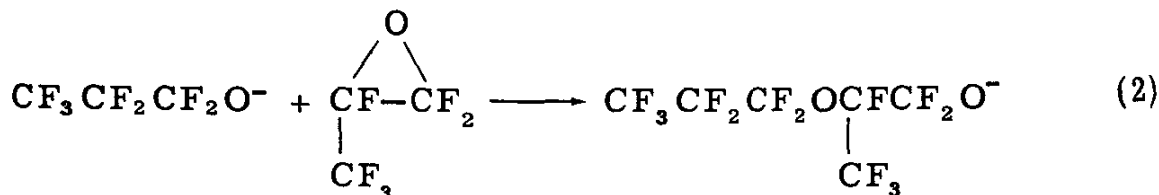undergoes nucleophilic attack at the more substituted carbon atom [2].

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*Contribution No. 250.

Fluoride ion opens the epoxide ring to give the n-perfluoropropoxide which can be isolated in the same manner as cesium trifluoro-methoxide [3].

$$F^- + \underset{\underset{CF_3}{|}}{CF}\overset{\overset{O}{/\backslash}}{-}CF_2 \longrightarrow CF_3CF_2CF_2O^- \tag{1}$$
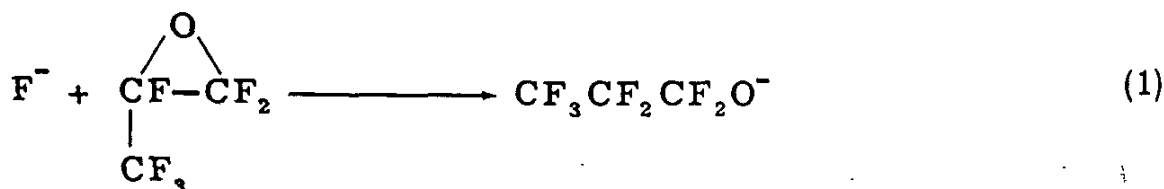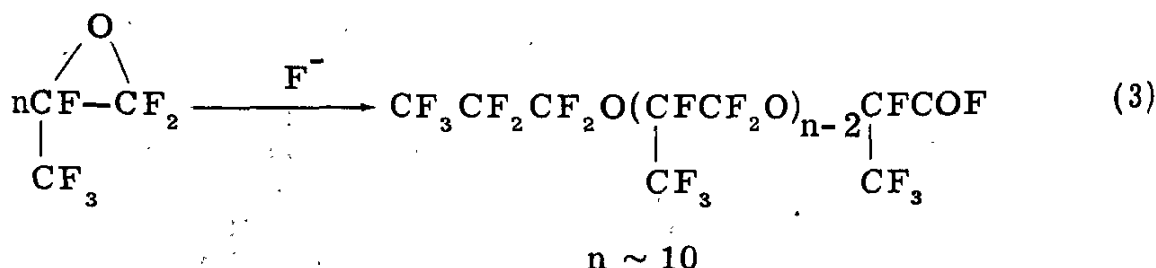
Under some conditions this alkoxide eliminates fluoride ion to yield perfluoropropionyl fluoride [4].

The alkoxide may react with another HFPO molecule to produce the alkoxide corresponding to the dimer of HFPO [5].
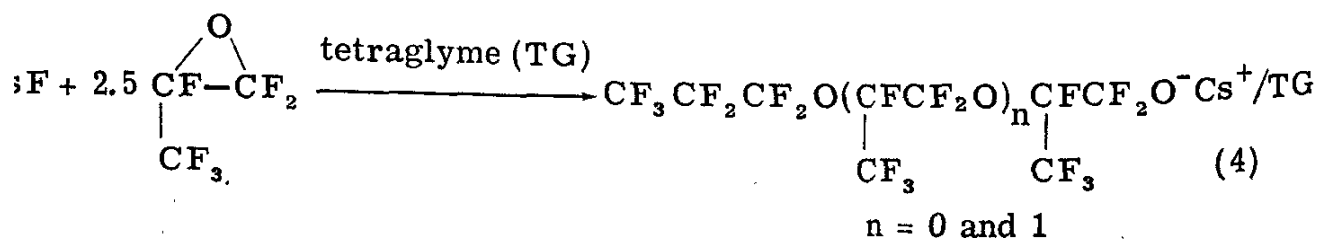
$$CF_3CF_2CF_2O^- + \underset{\underset{CF_3}{|}}{CF}\overset{\overset{O}{/\backslash}}{-}CF_2 \longrightarrow CF_3CF_2CF_2O\underset{\underset{CF_3}{|}}{C}FCF_2O^- \tag{2}$$

A number of metal fluorides and quaternary salts may be used in a variety of solvents to prepare other oligomers of this series [6].

$$n\underset{\underset{CF_3}{|}}{C}F\overset{\overset{O}{/\backslash}}{-}CF_2 \xrightarrow{F^-} CF_3CF_2CF_2O(\underset{\underset{CF_3}{|}}{C}FCF_2O)_{n-2}\underset{\underset{CF_3}{|}}{C}FCOF \tag{3}$$
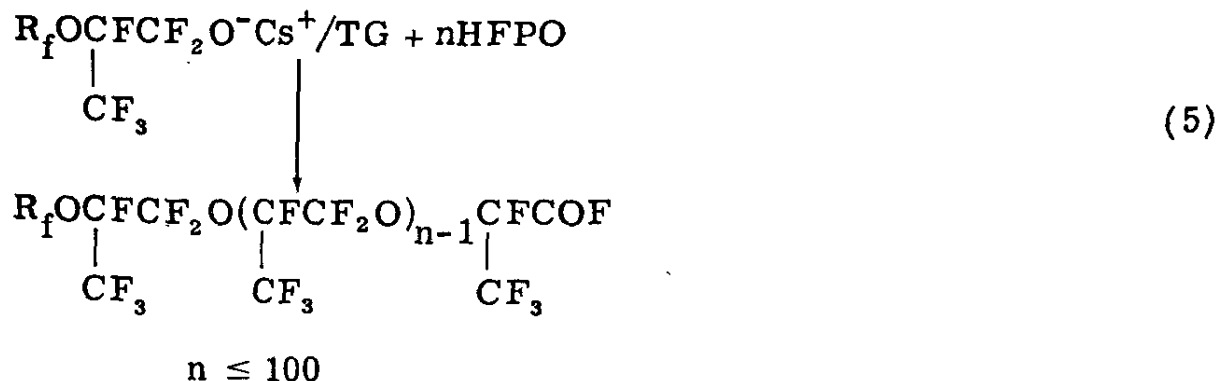
$$n \sim 10$$

Low molecular weight ($\overline{MW}$) polymers can be prepared with alkali metal fluorides in dimethyl ethers of oligomer ethylene glycols [7]. The preparation of higher molecular weight polymers with n (Eq. 3) as high as 100 can be achieved [8].

One process for preparing polymers of this molecular weight involves formation of a liquid catalyst [9] which provides for alkoxide rather than fluoride ion initiation. An example of these liquid compositions is that derived from reacting cesium fluoride, tetra-ethylene glycol dimethyl ether (tetraglyme, TG), and a limited amount of HFPO.

$$;F + 2.5 \underset{\underset{CF_3}{|}}{CF}\overset{\overset{O}{/\backslash}}{-}CF_2 \xrightarrow{\text{tetraglyme (TG)}} CF_3CF_2CF_2O(\underset{\underset{CF_3}{|}}{C}FCF_2O)_n\underset{\underset{CF_3}{|}}{C}FCF_2O^-Cs^+/TG \tag{4}$$

$$n = 0 \text{ and } 1$$

The initiator of Eq. (4) is then used in semibatch or continuous operation involving dilution with an appropriate solvent, additions of monomer at specified rates, control of temperature of the polymerization mixture, recycle of certain solvents, and withdrawal of crude polymer.

$$
\begin{array}{c}
R_fOCFCF_2O^-Cs^+/TG + nHFPO \\
\quad | \qquad\qquad\qquad | \\
\quad CF_3 \qquad\qquad\qquad | \\
\qquad\qquad\qquad\qquad\quad \downarrow \\
R_fOCFCF_2O(CFCF_2O)_{n-1}CFCOF \\
\quad | \qquad\qquad | \qquad\qquad | \\
\quad CF_3 \qquad\quad CF_3 \qquad\quad CF_3
\end{array}
\qquad (5)
$$

$$n \le 100$$

Consideration of the repeat-unit structure of poly-HFPO suggests that these polymers should have outstanding properties. Perfluorination imparts high temperature stability as well as inertness to most chemical reagents, while ether linkages increase polymer backbone flexibility and lead to good low temperature properties. Such characteristics are exhibited by fluorine-endcapped poly-HFPO [10-12].

EXPERIMENTAL AND RESULTS

We have conducted experiments to study further the mechanistic features of the polymerization of HFPO with both monofunctional and difunctional initiators.

Monofunctional Catalysts

A batch of low molecular weight ($\overline{MW}$) polymer was carefully distilled to give 44 fractions of the various oligomers. Each fraction consisted mainly of a mixture of three adjacent oligomers as determined by vapor phase chromatography (VPC). Analytically pure samples of the dimer through heptamer HFPO acyl fluorides were obtained by preparative scale VPC. These samples were stored in a dry box to prevent hydrolysis by atmospheric moisture.

^{19}F NMR spectra were taken on the purified oligomers and, from the areas of the absorptions, data similar to that shown in Table 1 were obtained. We were thus able to assign specific absorptions to the fluorine groupings as shown in Fig. 1. Anhydrous CsF as well as

TABLE 1. ^{19}F NMR Data for HFPO Acyl Fluorides

Absorption position[a]	Integrated absorption area	
	Hexamer[b]	Heptamer[c]
-25.7	1	1
+80.58	20	25
82.1	5	5
82.7	3	3
130.14	2	2
131.0	1	1
145.0	4	5
	36	42

[a] ppm from $CFCl_3$.
[b] $C_{18}F_{36}O_6$.
[c] $C_{21}F_{42}O_7$.
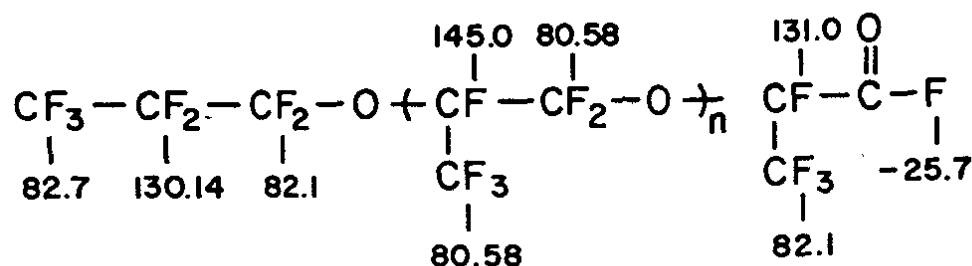
FIG. 1. ^{19}F NMR absorptions (ppm from $CFCl_3$) for HFPO oligomer acyl fluorides.

sodium-dried tetraglyme were stored in an inert atmosphere dry box where further manipulations were carried out.

Thorough mixing of an oligomer acyl fluoride ($\overline{MW} < 2000$), CsF, and TG leads to one phase solutions when the molar ratios are 1.0:1.0: > 2. Atomic absorption analyses of the resulting clear solutions gave the concentration of active alkoxide end groups. This general technique was used to prepare alkoxide solutions from pure HFPO acyl fluoride oligomers, oligomer mixtures, and a variety of other fluorinated acyl fluorides. Figure 2 illustrates the changes
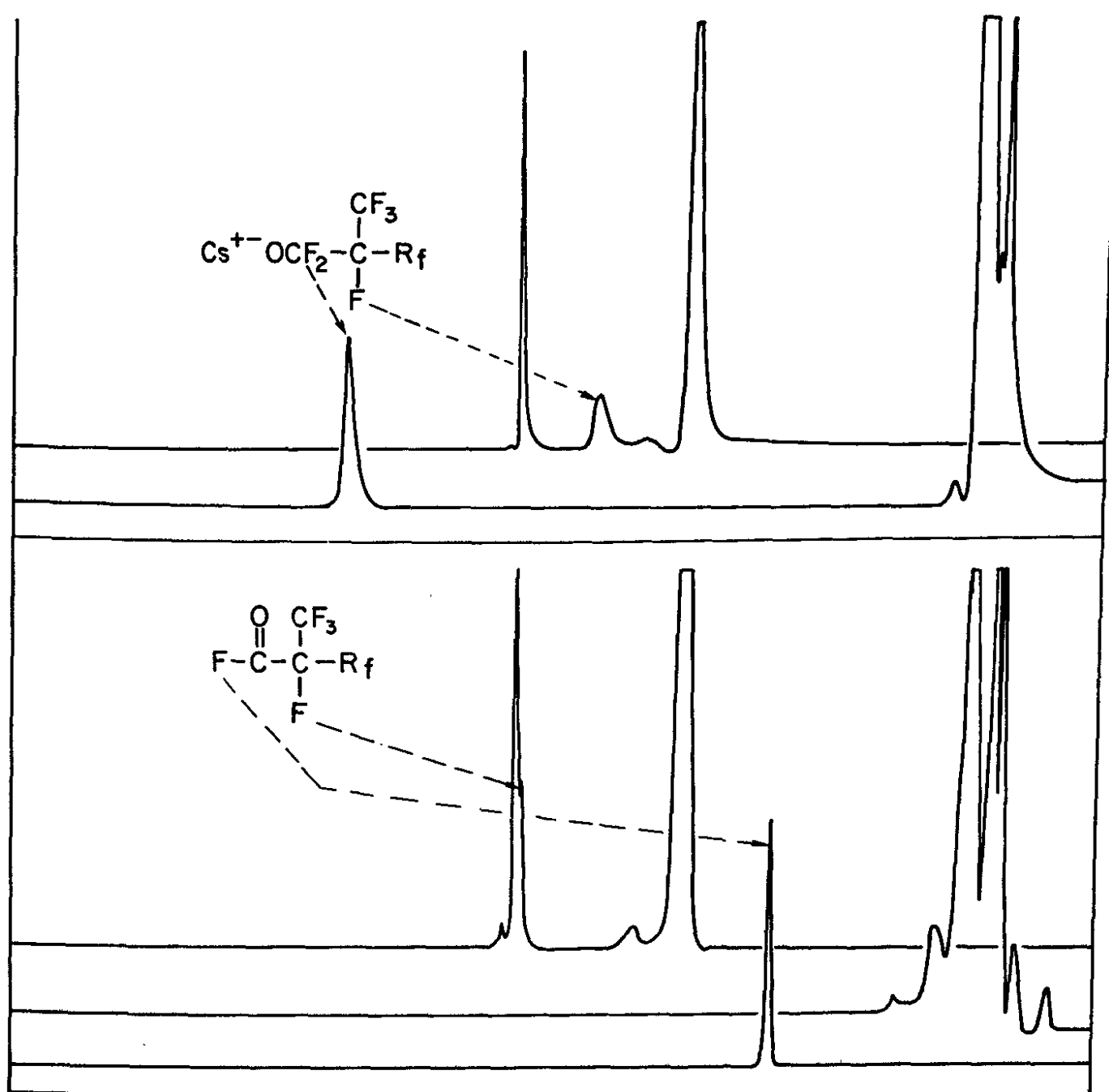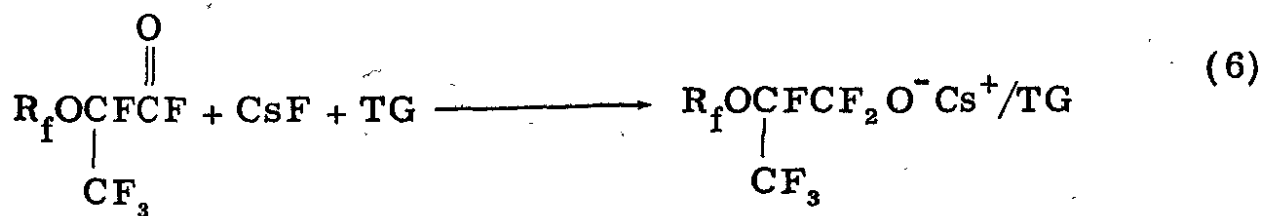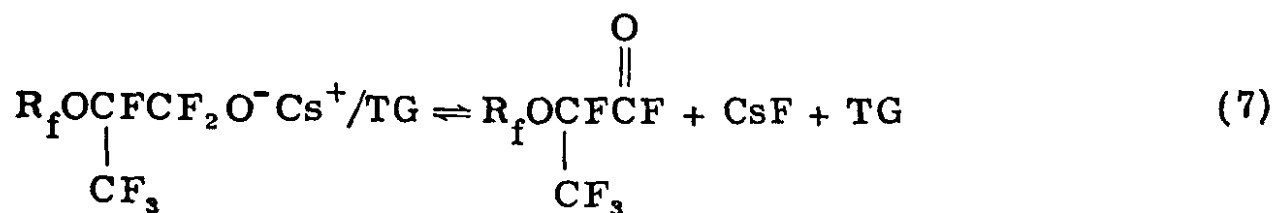
FIG. 2. ^{19}F NMR of a monofunctional HFPO acyl fluoride and its corresponding cesium alkoxide.

observed by ^{19}F NMR when acyl fluorides are converted to cesium alkoxide solutions.

$$R_f OCFCF + CsF + TG \longrightarrow R_f OCFCF_2 O^- Cs^+/TG \qquad (6)$$

A temperature-dependent ^{19}F NMR study over the range -40 to +80°C was carried out with TG solutions of the cesium alkoxides of HFPO dimer and trimer in order to investigate the equilibrium shown, in general, by

$$R_fOCFCF_2O^-Cs^+/TG \rightleftharpoons R_fOCFCF + CsF + TG \qquad (7)$$

$$| \qquad \qquad \overset{O}{\overset{\|}{|}}$$
$$CF_3 \qquad \qquad CF_3$$

No changes conforming to those predicted from Fig. 2 were found after short times, even at +80°. This is not too surprising in view of the reported stability of cesium trifluoromethoxide at this temperature [3].

We did find that these alkoxide solutions precipitated CsF and produced both a heavier fluorocarbon layer and lighter TG liquid layer when heated to 105°. The fluorocarbon layer was almost entirely acyl fluoride ($5.35\,\mu$). On cooling the three components and mixing again at room temperature, the acyl fluoride IR band virtually disappeared.

From this evidence we see that the equilibrium lies far to the side of these alkoxides (Eq. 7) at room temperature, but that some acyl fluoride may be present.

Monofunctional Polymerization

Polymerizations of HFPO were carried out under dry nitrogen using jacketed four-neck round bottom reaction vessels. A pre-determined amount of a liquid catalyst was accurately weighed into the vessel using a tared hypodermic syringe. A coolant from a circulating constant temperature bath was pumped through the jacket of the vessel so as to cool the stirred liquid to the desired temperature. Dry hexafluoropropylene (HFP) was condensed into the pot and mixed well with the viscous catalyst solution. HFPO was introduced through calibrated metering equipment. After the desired amount of HFPO had been added, stirring was continued for at least one hour to ensure complete reaction. After removal of the cold condenser from the vessel, the HFP was boiled off in vacuo as the pot temperature was brought to room temperature. Careful weighing of the off-gases and product showed that better than 99% material balance was achieved and that all the HFPO was consumed in polymer formation.

Under some conditions 10 to 15% less HFP off-gas was recovered than originally added, while the polymer mixture weighed a cor-responding amount more than the sum of liquid catalyst plus HFPO.

Dimers and trimers of HFP were isolated from those polymer mixtures. The polymerization may be run using these HFP oligomers as diluents, but HFP is preferred since higher $\overline{MW}$ polymers are obtained.

A run typical of small-scale polymerizations involved an initial charge of 4.5 mmoles of cesium alkoxide catalyst and 35 g of HFP, to which 162 g of HFPO was added over a 30-hr period. A small layer of TG slowly separated from the final product. The theoretically $\overline{MW}$ for this polymer was 37,500. Several techniques (VPC, IR, NMR, VPO, UV, titrimetry, viscosity) have been developed to determine the $\overline{MW}$ of HFPO polymers. This one, analyzed by the 5.35 μ IR band of the acyl fluoride, showed a $\overline{MW}$ of 15,500. We can thus calculate a chain transfer parameter (C.T. = $\overline{MW}_{theory}/\overline{MW}_{actual}$) of 2.42 for this run, which means that 1.42 moles of new chains were created during the run for every mole of initiator used.

One polymerization was carried out with 4.66 mmoles of a TG solution of cesium HFPO trimer alkoxide, 42 g of HFP solvent, and continuous addition of 277 g of HFPO over a period of 50 hr. Samples were removed at intervals during the polymerization in order to follow the $\overline{MW}$ as a function of time and the amount of monomer added. Figure 3 shows the relationship between $\overline{MW}$ and time of continuous
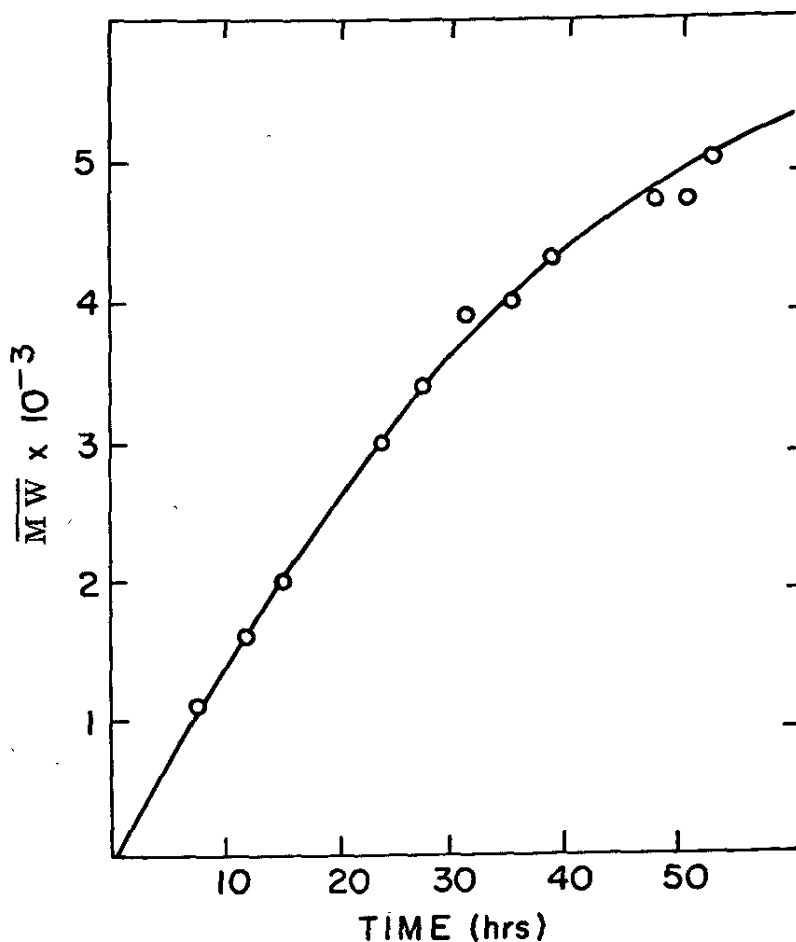

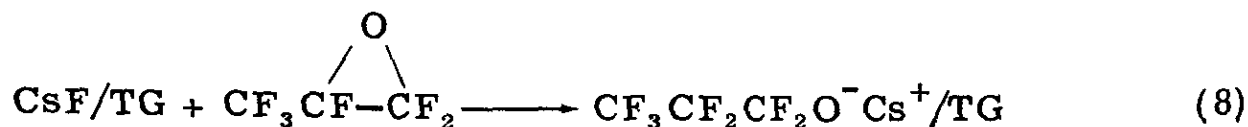FIG. 3. HFPO polymerization using cesium HFPO trimer alkoxide initiator.

addition and points out the severe limitation on $\overline{MW}$ by chain transfer. A value of C.T. = 8.0 was found at 7 hr, increasing to only 11.9 at the end of 50 hr. This suggests that most of the chain transfer takes place early into the polymerization—perhaps even at the onset of monomer addition.

The living anionic nature of these polymerizations can be illustrated by stopping monomer addition, allowing a short time for complete reaction, and then restarting the addition. Analyses done after stopping monomer addition and again some time after resuming monomer addition will show a distinct increase in $\overline{MW}$ as well as complete uptake of the second portion of monomer. This process may be repeated at will.
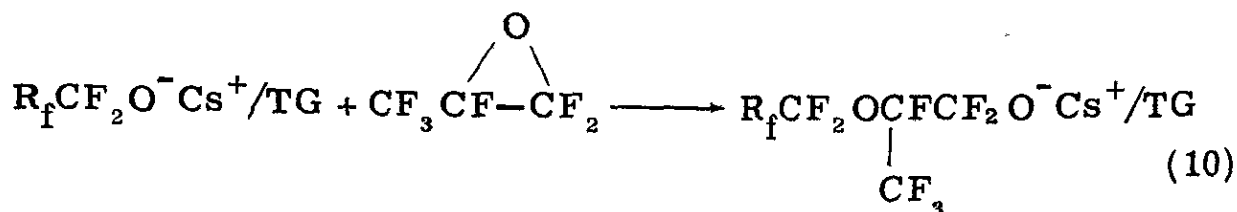
Monofunctional Mechanism

From the literature information mentioned earlier and from the results presented here, we can propose a mechanism for the polymerization:

Initiation:

$$CsF/TG + CF_3\overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CF-CF_2}} \longrightarrow CF_3CF_2CF_2O^-Cs^+/TG \qquad (8)$$

Propagation:

$$CF_3CF_2CF_2O^-Cs^+/TG + nCF_3\overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CF-CF_2}} \longrightarrow R_fCF_2O^-Cs^+/TG \qquad (9)$$

$$R_fCF_2O^-Cs^+/TG + CF_3\overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CF-CF_2}} \longrightarrow R_fCF_2\underset{\displaystyle \underset{\displaystyle CF_3}{|}}{OCFCF_2}O^-Cs^+/TG \qquad (10)$$

Chain Termination:

$$R_fCF_2\underset{\displaystyle \underset{\displaystyle CF_3}{|}}{OCFCF_2}O^-Cs^+/TG \rightleftharpoons R_fCF_2\underset{\displaystyle \underset{\displaystyle CF_3}{|}}{OCFCOF} + CsF/TG \qquad (11)$$

Reinitiation:

$$CsF/TG \longrightarrow Step\ (8)$$

CsF Termination:

$$CsF/TG \rightleftharpoons CsF + TG \tag{12}$$

$$CsF/TG + CF_3CF=CF_2 \rightleftharpoons CF_3\underset{\underset{CF_3}{|}}{C}FCs/TG \tag{13}$$
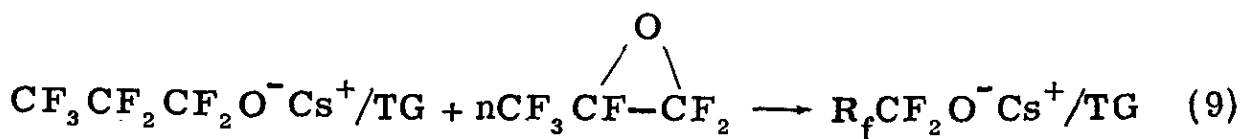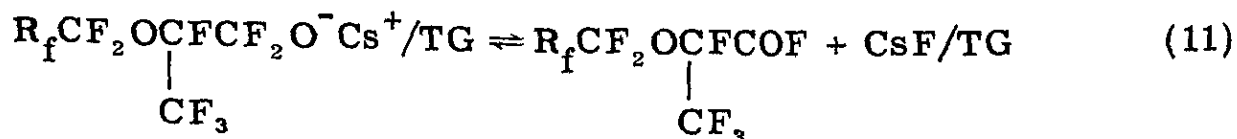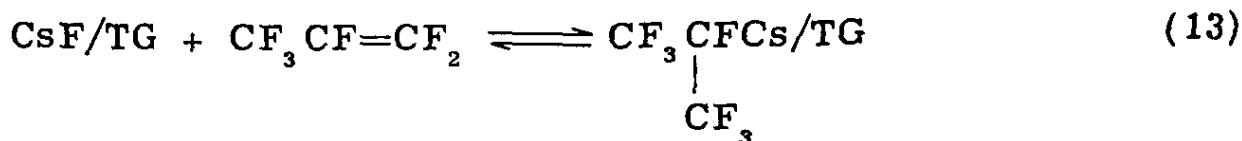
If a preformed cesium alkoxide solution is used to prepare polymer, the sequence begins at Eq. (10) with alkoxide attacking monomer to lead stepwise to higher and 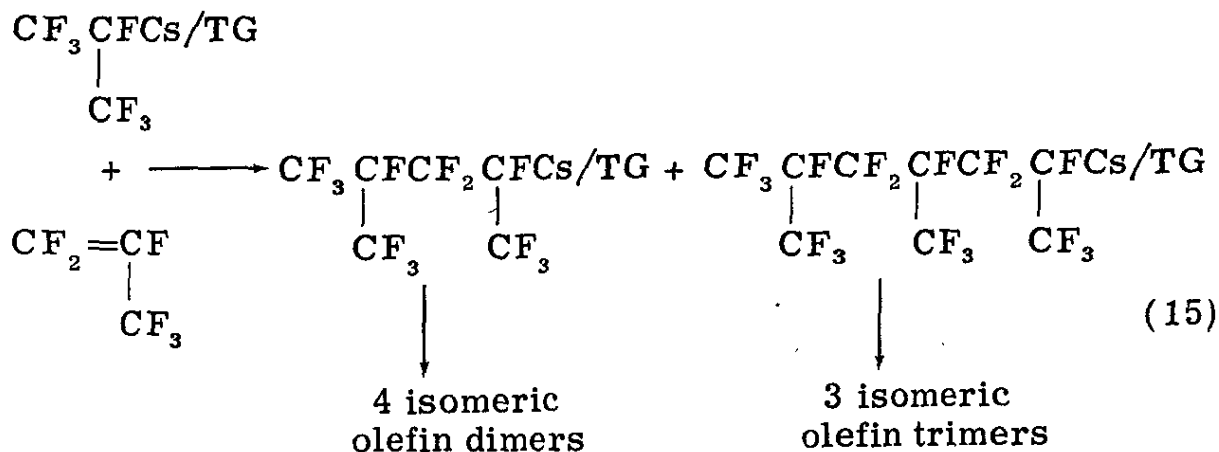higher $\overline{MW}$ polymer. Every growing molecule has a very small but finite chance of terminating the growing end by elimination of CsF to produce the acyl fluoride end group polymer as shown in Eq. (11). The soluble CsF (designated as CsF/TG) may then take part in any of at least four reactions, one of which is simple addition back to acyl fluoride to regenerate active alkoxide (reverse direction in Eq. 11).

Another alternative produces new chains by initiation of monomer as shown in Eq. (8). This chain transfer process severly limits the molecular weight since the new active alkoxide leads directly to new polymer molecules as in Eq. (9).
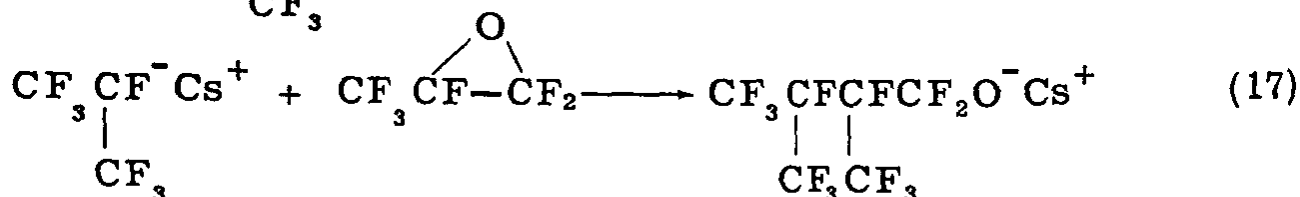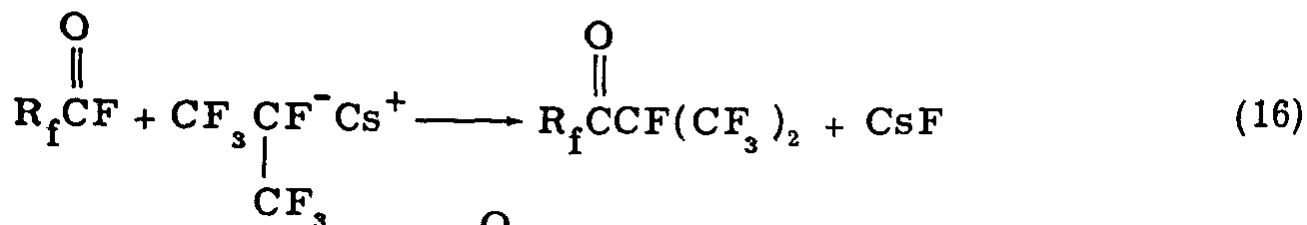
The soluble CsF may be deactivated as in Eq. (12) by precipitation from the predominantly fluorocarbon medium. Another route which deactivates CsF/TG is that by which fluoride ion adds to the HFP solvent (Eq. 13). By analogy to Miller's work on the stable covalent adduct of AgF to HFP [13], it is possible that the cesium alkyl is of moderate stability at the reaction temperature of -32°.

$$AgF + CF_3CF=CF_2 \longrightarrow CF_3\underset{\underset{CF_3}{|}}{C}FAg \tag{14}$$
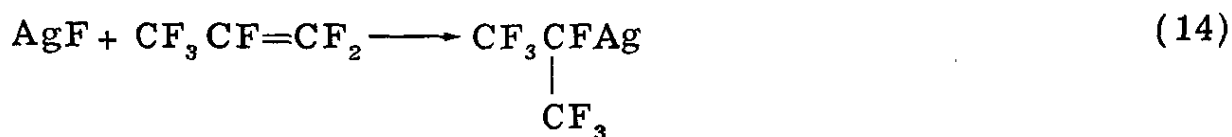
The alkyl-cesium is probably less covalent and/or less stable than the corresponding silver alkyl as is indicated by the production of the dimers and trimers of HFP [14].

$$\underset{\underset{CF_3}{|}}{CF_3CFCs/TG} + \underset{\underset{CF_3}{|}}{CF_2=CF} \longrightarrow \underset{\underset{CF_3}{|}\quad\underset{CF_3}{|}}{CF_3CFCF_2CFCs/TG} + \underset{\underset{CF_3}{|}\quad\underset{CF_3}{|}\quad\underset{CF_3}{|}}{CF_3CFCF_2CFCF_2CFCs/TG} \tag{15}$$

4 isomeric
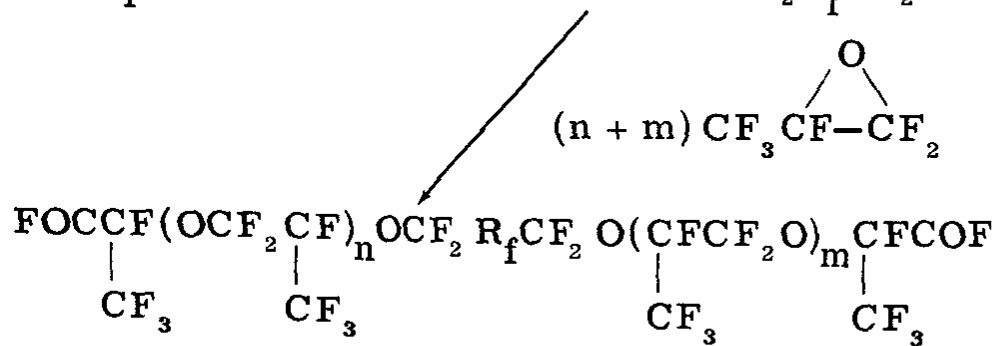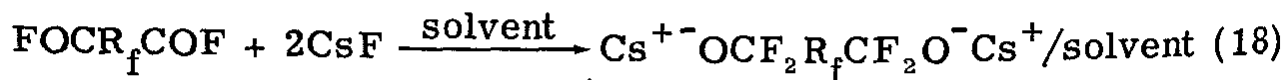olefin dimers   3 isomeric
                                       olefin trimers

Under our polymerization conditions we do not observe ketones or HFP-initiated polymers as one might expect according to

$$R_fCF + CF_3\overset{-}{C}F\,Cs^+ \longrightarrow R_f\overset{O}{\overset{\|}{C}}CF(CF_3)_2 + CsF \qquad (16)$$

with the $\overset{O}{\overset{\|}{C}}$ on R_fCF and CF_3 substituent on the carbanion.

$$CF_3\overset{-}{C}F\,Cs^+ + CF_3\overset{O}{\overset{/\ \backslash}{CF-CF_2}} \longrightarrow CF_3CFCFCF_2O^-Cs^+ \qquad (17)$$

with CF_3 on the first carbanion and $CF_3\,CF_3$ substituents on the product.

The beneficial role played by HFP arises not only from its ability to solubilize most of the polymer produced (thereby reducing viscosity and aiding heat transfer for the exothermic polymerization), but also from its ability to capture active fluoride ions which otherwise could lead to chain transfer. The fact that HFP dimers or trimers are less effective in $\overline{MW}$ build-up is explained by the extreme difficulty of fluoride ion addition to the thermodynamically favored internally substituted double bonds.

Difunctional Catalysts

Processes for the preparation of polymers from HFPO with two acyl fluoride end groups (difunctional) have been reported [15, 16] and appear to involve the in situ generation of bis(alkoxides).

$$FOCR_fCOF + 2CsF \xrightarrow{\ \text{solvent}\ } Cs^{+-}OCF_2R_fCF_2O^-Cs^+/\text{solvent} \quad (18)$$

$$(n + m)\,CF_3\overset{O}{\overset{/\ \backslash}{CF-CF_2}}$$

$$FOCCF(OCF_2CF)_nOCF_2\,R_fCF_2\,O(CFCF_2O)_mCFCOF$$
$$\quad\ \ CF_3 \qquad\ CF_3 \qquad\qquad\ CF_3 \qquad\ CF_3$$
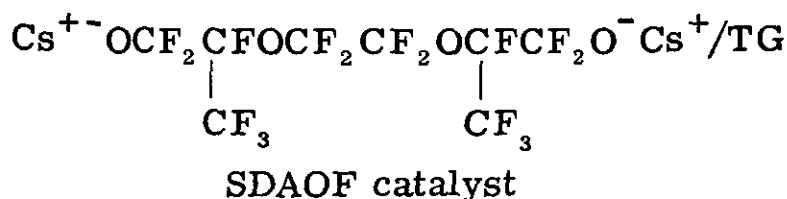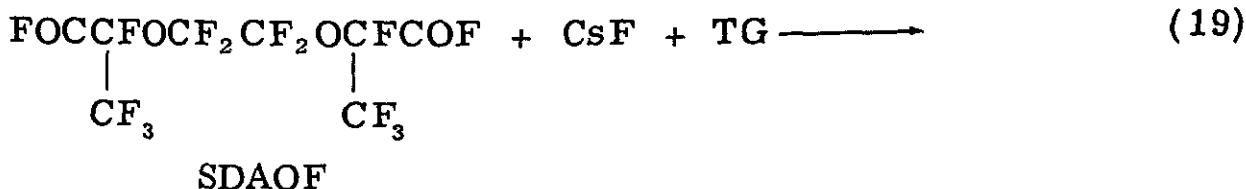
$$n + m \simeq 100$$

We have investigated these reactions using several preformed cesium alkoxide solutions prepared from a number of bis(acyl) fluorides. Much of our work has been based on the symmetrical diadduct of HFPO with oxalyl fluoride (SDAOF).

$$\underset{\underset{\displaystyle CF_3}{|}}{FOCCFOCF_2CF_2OC}\underset{\underset{\displaystyle CF_3}{|}}{FCOF}$$
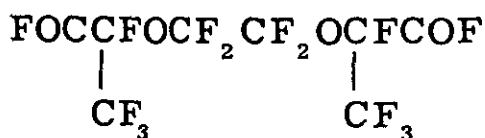
SDAOF

This compound has been reported [15] and was obtained in 20% yield by modifications of that procedure.

The bis(cesium) alkoxide can be prepared in TG solution in a manner similar to that previously described except that more solvent is required.

$$\underset{\underset{\displaystyle CF_3}{|}}{FOCCFOCF_2CF_2OC}\underset{\underset{\displaystyle CF_3}{|}}{FCOF} + CsF + TG \longrightarrow \qquad (19)$$

SDAOF

$$Cs^{+-}OCF_2\underset{\underset{\displaystyle CF_3}{|}}{CFOCF_2CF_2OC}\underset{\underset{\displaystyle CF_3}{|}}{FCF_2}O^-Cs^+/TG$$

SDAOF catalyst

Analysis by atomic absorption methods shows the liquid catalyst to have the theoretical cesium content. Figure 4 illustrates the ^{19}F NMR spectral changes that occur when reaction takes place as in Eq. (19) to produce the catalyst from SDAOF.

Difunctional Polymerization

This last initiator has been used to synthesize cleanly difunctional HFPO polymers using the technique described earlier. A typical difunctional polymerization employed 0.29 mole of the SDAOF initiator and 903 g of HFP, to which 820 g of HFPO was added. The product was a polymer of $\overline{MW}$ 3200 (vapor pressure osmometry), within experimental error (±3%) of the theoretical $\overline{MW}$ = 3300. No monofunctional polymer formed by fluoride initiation of monomer could be found by ^{19}F NMR.

Polymer Characterization

As previously mentioned, a number of methods have been used to determine the $\overline{MW}$ of monofunctional HFPO polymers. These techniques have been extended to the analysis of difunctional HFPO polymers which have the addition aspect of functionality.

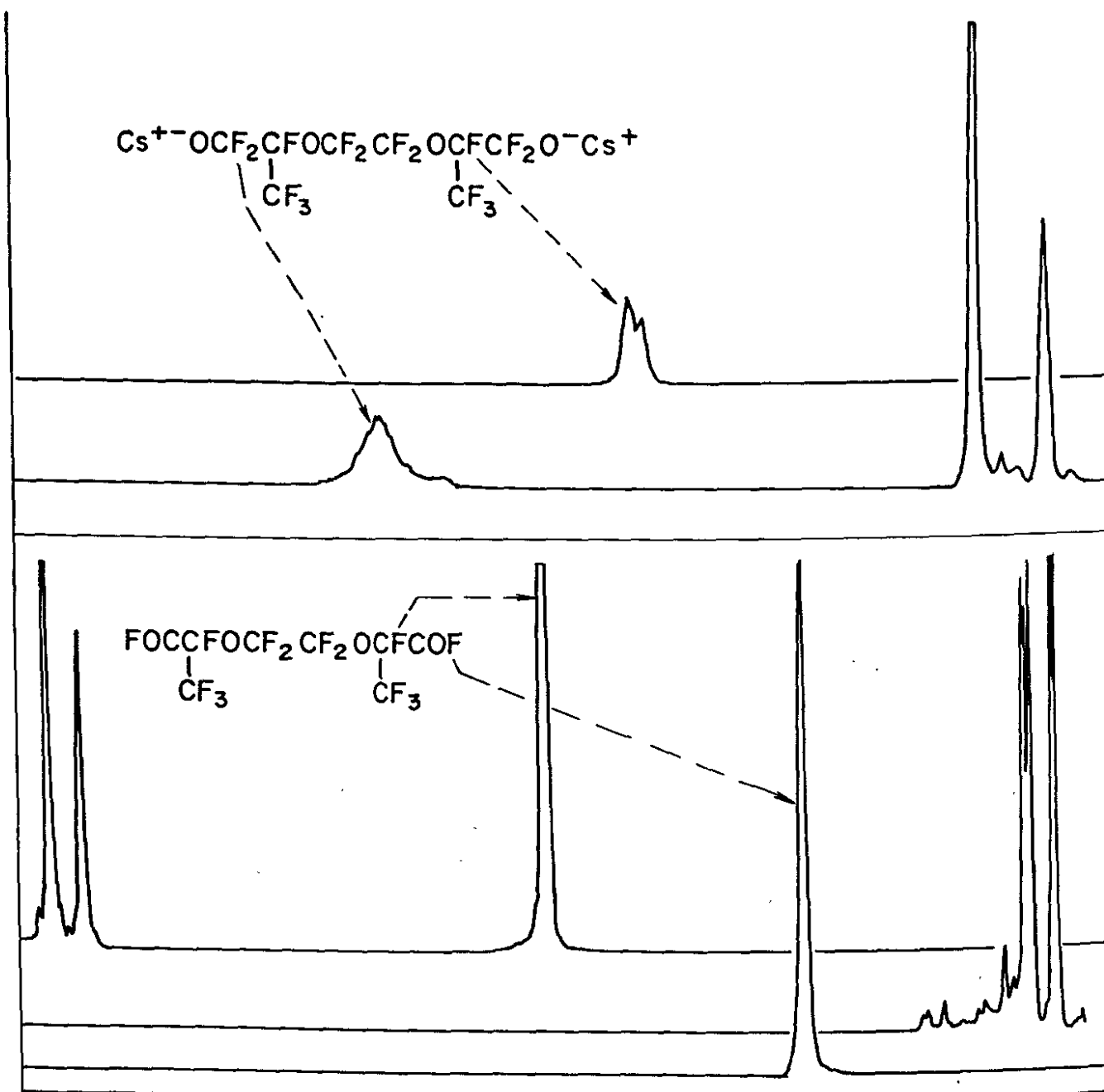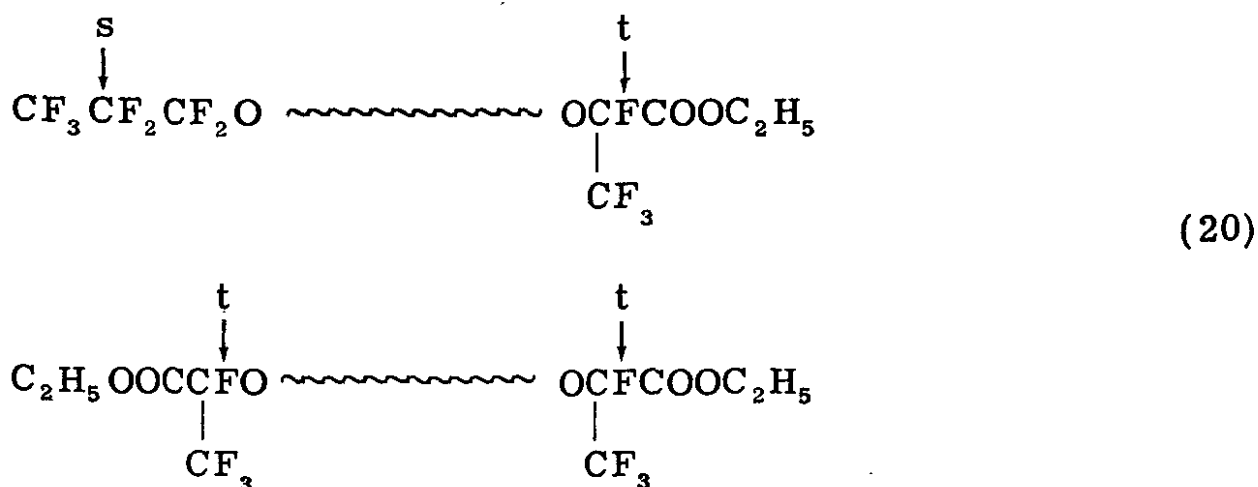Earlier it was pointed out that oligomer "triads" and oligomer

FIG. 4. ^{19}F NMR of a difunctional acyl fluoride (SDAOF) and its corresponding cesium alkoxide.

mixtures containing no material higher than the tetradecamer ($\overline{MW}$ = 2324) can be analyzed by VPC. The well-resolved peaks allow integrations for both acyl fluoride and ethyl ester end group oligomers so that a number of "standards" exist. These standards were used to define the extinction coefficients for the IR absorption at 5.35 μ (acyl fluoride) or 5.6 μ (ester). Weight-average molecular weights up to 25,000 can be determined with an error of about ±3% using the IR technique. In the case of difunctional polymers, the IR method gives an equivalent weight from which the $\overline{MW}$ can be calculated as described later.

Equivalent weights have also been determined by KOH/EtOH saponification of ethyl ester terminated polymers. A UV technique has been devised [17] to take advantage of the intense 233.5 mμ absorption of p-methoxybenzyl amide terminated poly-HFPO as another measure of equivalent weight. Vapor phase osmometry and viscometric procedures have also been used to determine $\overline{MW}$. We find that all the above techniques give comparable results.

The functionality of polymers has been studied by ^{19}F NMR. Consider an equimolar mixture of monofunctional and difunctional ethyl ester terminated polymers.

$$
\begin{array}{cc}
\text{s} & \text{t} \\
\downarrow & \downarrow \\
CF_3CF_2CF_2O \sim\!\!\sim\!\!\sim\!\!\sim & OCFCOOC_2H_5 \\
& | \\
& CF_3
\end{array}
$$

$$
\begin{array}{cc}
\text{t} & \text{t} \\
\downarrow & \downarrow \\
C_2H_5OOCCFO \sim\!\!\sim\!\!\sim\!\!\sim & OCFCOOC_2H_5 \\
| & | \\
CF_3 & CF_3
\end{array}
$$

(20)

The fluorine atoms labeled "s" (secondary) absorb at 131.56 ppm (reference = $CFCl_3$) and those labeled "t" (tertiary) absorb at 133.33 ppm in the ^{19}F NMR. Experimentally we find that these well-defined, separated, easily integrable peaks occur in the ratio 2.0:1.0 for monofunctional polymers and that no "s" peak exists in pure difunctional polymer from SDAOF. A mixture of these two types of the same polymer will have s/t ratios which can be converted to % difunctionality by

$$\% \text{ difunctionality} = \frac{t/s - 1/2}{t/s + 1/2} \times 100 \qquad (21)$$

Figure 5 illustrates the spectra observed at high amplitude in the region of interest for one partially and one almost completely difunctional polymer.

Molecular Weight, Functionality, and Time

That chain transfer limits the $\overline{MW}$ in the monofunctional polymerization prompted us to investigate the behavior of both $\overline{MW}$ and functionality as a function of time in a difunctional polymerization, using a constant continuous HFPO feed. Experimental conditions
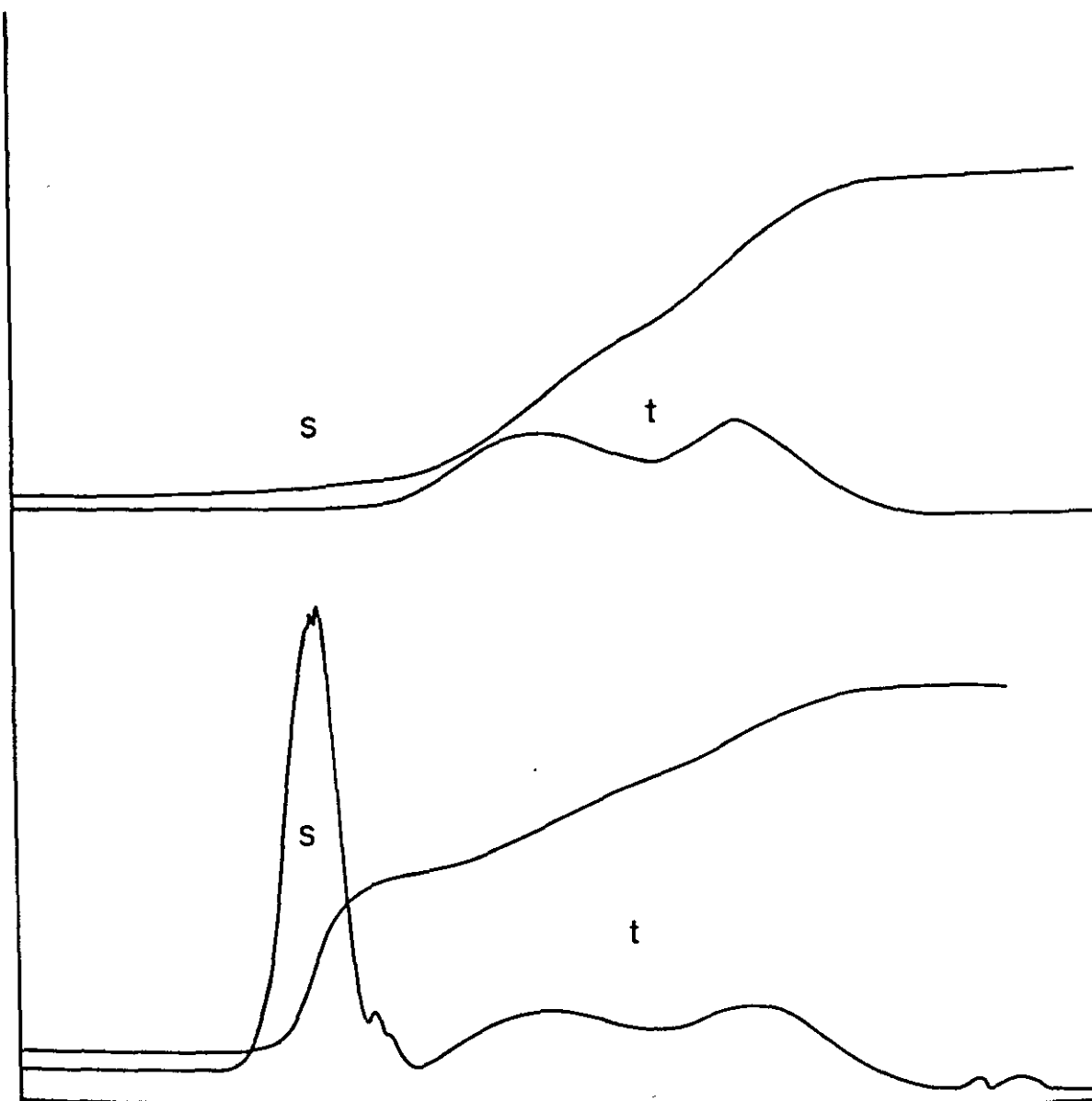
FIG. 5.   Partial expanded scale ^{19}F NMR of 33% difunctional poly-HFPO (bottom) and 95% difunctional poly-HFPO (top).   (Refer to Eq. 20 for the meanings of s and t.)

were chosen to allow formation of a theoretical $\overline{MW}$ 25,000 polymer and not to maintain complete difunctionality.   The amounts of materials used were 0.0416 mole of SDAOF initiator, 1601 g of HFP, and 999 g of HFPO. After 12 hr monomer addition was stopped, and the polymerization mixture cooled from -32°C down to -78°C and kept there for 8 hr.   After warming the mixture to -32°C, monomer addition was restarted and the polymerization was continued.

Sixteen samples (5 to 10 g each) were removed at random intervals from the polymerizing mixture and the HFP plus HFPO carried along were condensed and immediately returned to the reaction vessel.   Each sample was converted to the ethyl ester according to a standard technique

and carefully purified by multiple ether extractions, filtrations, and evaporations. These samples were analyzed by ^{19}F NMR to determine the functionality and by IR to obtain the equivalent weight. A "corrected $\overline{MW}$" ($\overline{MW}_c$) was then calculated by

$$\overline{MW}_c = (1 + \%d/100)(\overline{MW}_{IR}) \qquad (22)$$

The data obtained from these samples are shown in Table 2. Figures 6 and 7 display these data for $\overline{MW}_c$ vs time and % difunctionality vs time, respectively. From Fig. 6 it is obvious that the $\overline{MW}$ lags considerably behind the theoretical $\overline{MW}$ up to about 200 min, at which time it begins to increase very rapidly. Such an increase is

TABLE 2. Molecular Weight and Difunctionality for an HFPO Polymerization

Time (min)	$\overline{MW}_{IR}$ [a]	% Dif. [b]	$\overline{MW}_c$ [c]
191	770	95.3	1500
255	2270	94.4	4410
295	2630	90.7	5020
355	3010	85.7	5590
415	3420	79.5	6140
485	3660	73.2	6340
540	3870	64.4	6360
600	4140	61.9	6700
660	4420	57.8	6980
715	4520	55.2	7020
720	4800	51.6	7280
720[d]	4940	48.6	7340
820	5260	50.4	7910
905	5310	48.5	7880
960	5500	45.4	8000
960[e]	5660	41.2	8000

[a]Determined by absorption at 5.6 μ.
[b]Calculated by Eq. (21).
[c]Calculated by Eq. (22).
[d]Sample taken after holding at -78° for 8 hr.
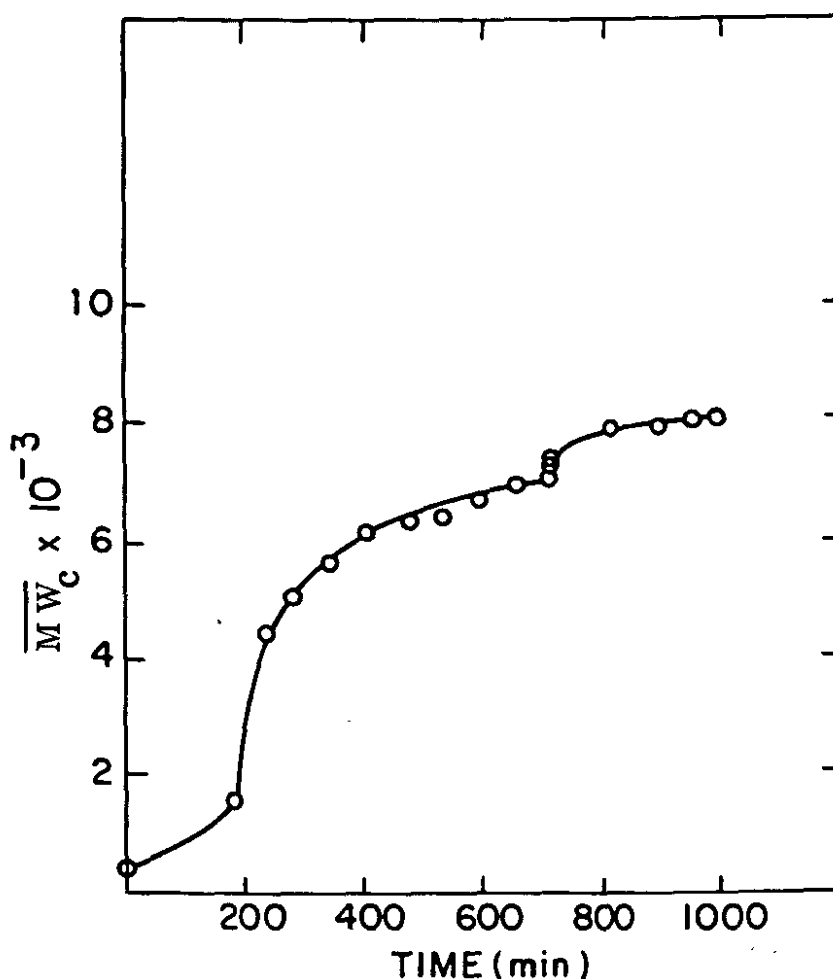[e]Sample taken 60 min after stopping HFPO addition.

FIG. 6. HFPO polymerization using difunctional initiator.

possible only if there is monomer accumulation during a slow initiation. The SDAOF catalyst solution is not initially completely miscible with the HFP diluent so that slow initiation may be caused by HFPO having to diffuse through the mass of viscous tetraglyme to find the active alkoxide end groups. Once the catalyst has added a few units of HFPO, the oligomers become more soluble in the HFP and monomer uptake is quite rapid as indicated by an abrupt evolution of heat. An alternate hypothesis is that the ionic end groups are aggregated in highly polar domains. The nonpolar HFPO would enter the regions slowly and only react with alkoxide end groups which break away from the clusters. On occasion, polymerizations have given water-clear, one-phase mixtures when the $\overline{MW}$ is about 4000 to 6000. At about 300 min into this run the severe effect of chain transfer on the $\overline{MW}$ (and on difunctionality) was noted.

From the difunctionality measurements it is possible to develop a formula (Eq. 23) to calculate the pseudo-first-order rate constant for chain transfer (k_t). This formula utilizes the ^{19}F NMR ratios (R = t/s) discussed earlier.
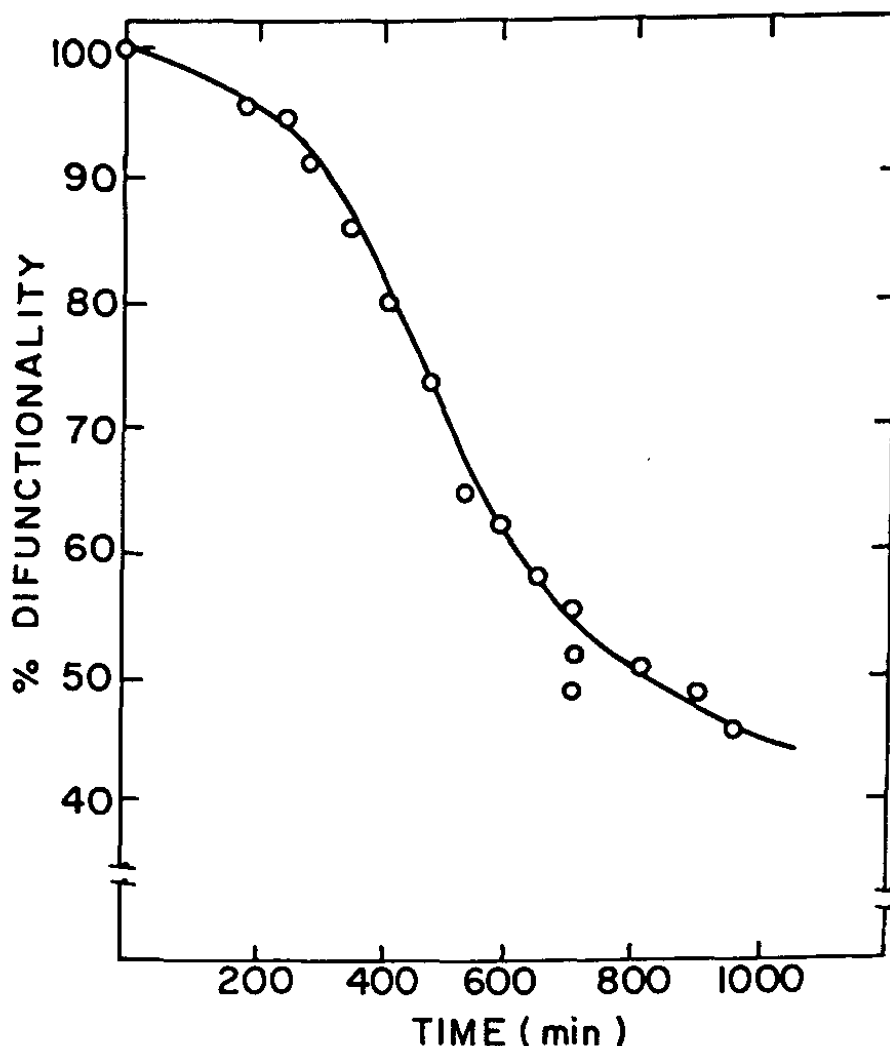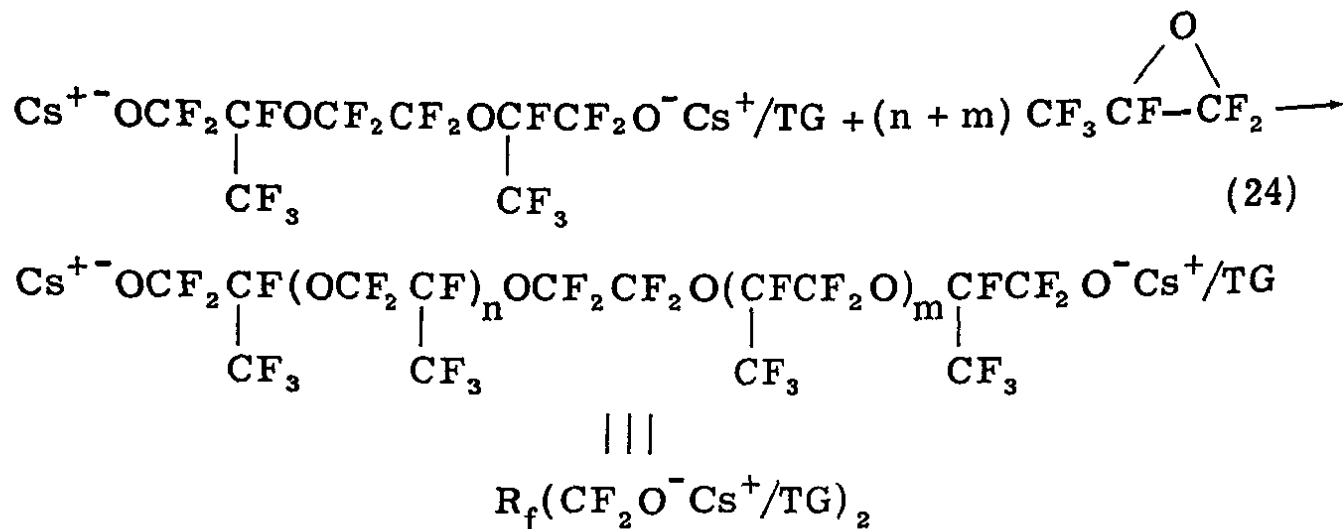
FIG. 7. HFPO polymerization using difunctional initiator.

$$k_t = \frac{1}{(2R - 1)t} \qquad (23)$$

Point by point calculation of k_t's led to an average $k_t = 7.9 \times 10^{-6}$ sec^{-1}. The assumption that the number of alkoxide ends (determined by cesium analysis) is constant at all times leads to slightly lower values for k_t for the first four points taken. The initiator is not completely soluble at the beginning of the reaction so that not all the active cesium alkoxides ends are able to participate in the polymerization. As the polymerization proceeds, all the initiator does dissolve and the assumption becomes valid. Calculations of k_t from the final difunctionality obtained for 20 other polymerizations done under similar conditions gave an average value of 8.4×10^{-6} sec^{-1}.
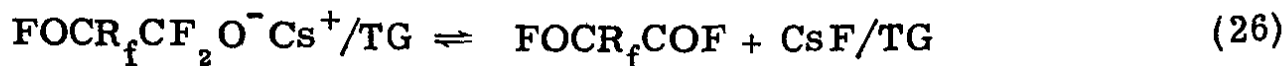
Difunctional Mechanism

The mechanism for the polymerization of HFPO with the difunctional SDAOF initiator is similar to that for monofunctional polymerization. The basic modification is the two-stage chain termination.
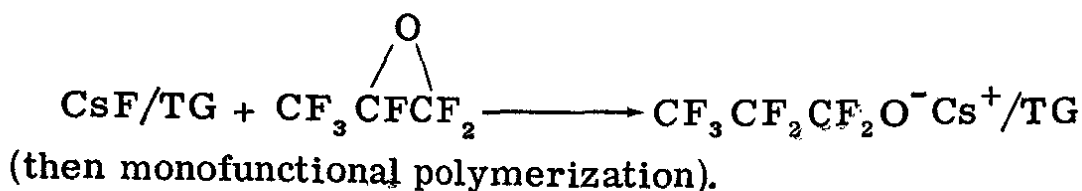
Difunctional Initiation and Propagation:

$$Cs^{+-}OCF_2CFOCF_2CF_2OCFCF_2O^-Cs^+/TG + (n + m) \; CF_3CF\overset{O}{\overbrace{-}}CF_2 \longrightarrow$$

$$\overset{|}{CF_3} \qquad\qquad \overset{|}{CF_3}$$

$$Cs^{+-}OCF_2CF(OCF_2CF)_nOCF_2CF_2O(CFCF_2O)_mCFCF_2O^-Cs^+/TG$$

$$\overset{|}{CF_3} \quad \overset{|}{CF_3} \qquad\qquad \overset{|}{CF_3} \quad \overset{|}{CF_3}$$

$$|||$$

$$R_f(CF_2O^-Cs^+/TG)_2$$

Chain Termination:

$$R_f(CF_2O^-Cs^+/TG)_2 \;\rightleftharpoons\; FOCR_fCF_2O^-Cs^+/TG + CsF/TG \qquad (25)$$

$$FOCR_fCF_2O^-Cs^+/TG \;\rightleftharpoons\; FOCR_fCOF + CsF/TG \qquad (26)$$

Reinitiation of Monomer:

$$CsF/TG + CF_3CF\overset{O}{\overbrace{-}}CF_2 \longrightarrow CF_3CF_2CF_2O^-Cs^+/TG$$

(then monofunctional polymerization).

Consideration of the kinetics of this mechanism leads to the following expressions [18]:

$$\overline{DP}_D = \frac{2P}{T}(1 - e^{-Tt}) \qquad (27)$$

$$\overline{DP}_M = \frac{P}{T}(1 - \frac{1 - e^{-Tt}}{Tt} \qquad (28)$$

$$\overline{DP}_{D+M} = \frac{P}{T + \frac{1}{2t}} \qquad (29)$$

$$wf_D = \frac{1 - e^{-Tt}}{Tt} \qquad (30)$$

where $\overline{DP}_D$ is the average degree of polymerization of difunctional molecules, $\overline{DP}_M$ is the average degree of polymerization of monofunctional molecules, $\overline{DP}_{D+M}$ is the average degree of polymerization of all molecules, wf_D is the weight fraction of difunctional molecules, P is the pseudo-first-order propagation rate constant, T is the pseudo-first-order termination rate constant, and t is the time in seconds.

Computer calculations indicate that, because of initial partial solubility of initiator, an "adjusted" time is preferred to the actual sample times given in Table 2. Hence about 10,000 sec should be subtracted from the data so that the adjusted polymerization t = 0 corresponds to actual t $\cong$ 167 min. "Adjusted" time and the pseudo-first-order termination rate constant (T) of 8×10^{-6} sec^{-1} generates the weight fraction of difunctional molecules by Eq. (30). This weight fraction can be converted to % difunctionality which agrees with the observed data.
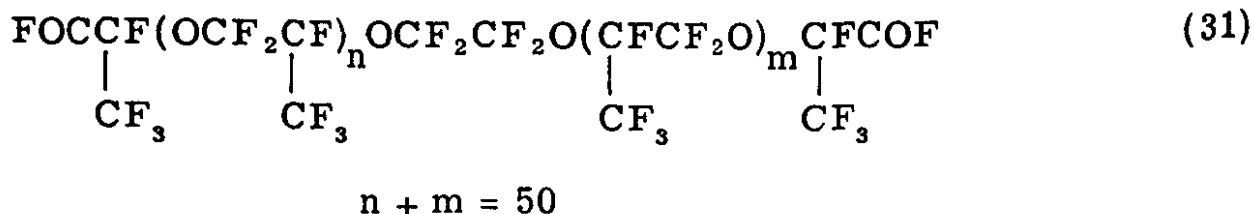
Similarly, Eq. (29) can be used to produce $\overline{DP}_{D+M}$ if a choice of the pseudo-first-order propagation rate (P) is made. A value of 8×10^{-4} sec^{-1} for P generates $\overline{DP}_{D+M}$ values which agree with the observed $\overline{DP}_{D+M}$.

It is interesting to note the limiting values of Eqs. (27)-(30) as time approaches infinity; these are $\overline{DP}_D \rightarrow 2P/T$, $\overline{DP}_M \rightarrow P/T$, $\overline{DP}_{D+M} \rightarrow P/T$, $wf_D \rightarrow 0$. With these limits and under the specific conditions given, the difunctional molecules can be expected to grow to no more than $\overline{MW}$ 33,000 ($\overline{DP}_D$ = 200) and the monofunctional molecules to grow to only $\overline{MW}$ 16,500 ($\overline{DP}_M$ = 100). The functionality will slowly decrease from completely difunctional to almost completely monofunctional if monomer is added for long enough periods. One limiting factor on production of monofunctional polymer is the presence of HFP which traps fluoride ion and prevents the formation of new chains.
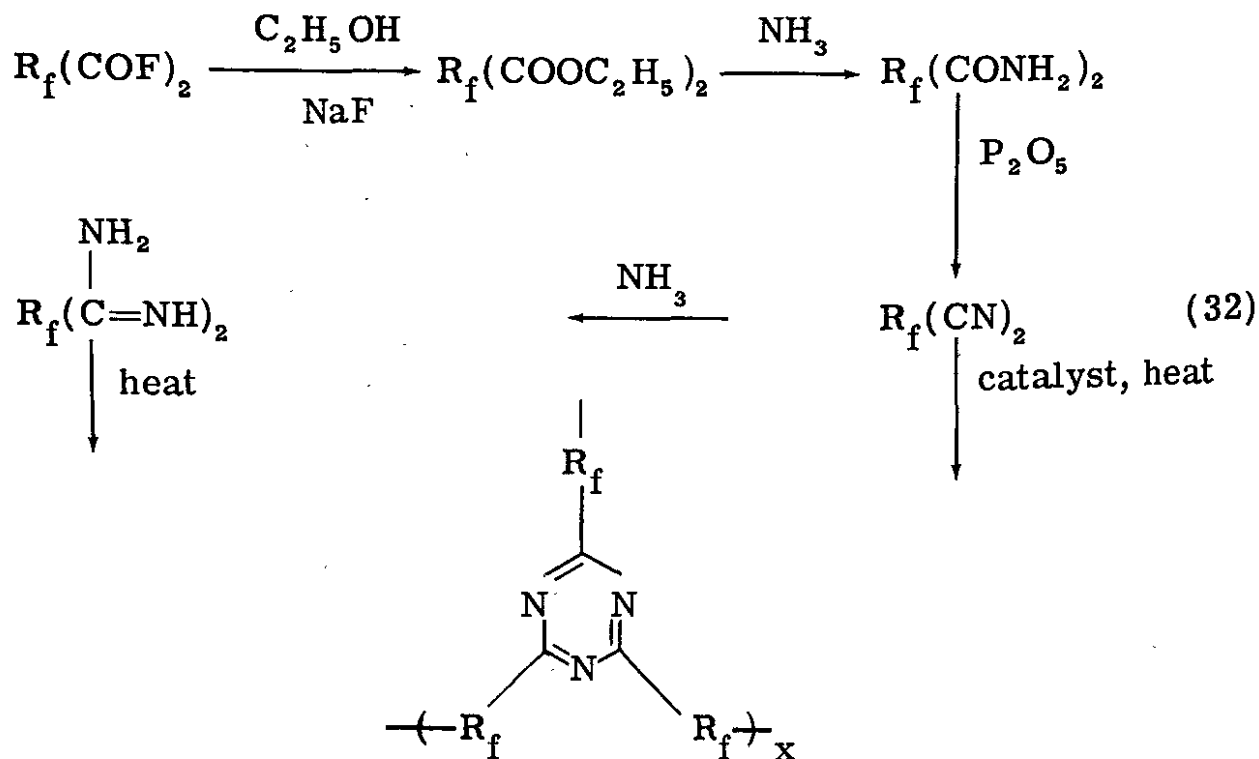
Cleanly Difunctional Polymers and Derivatives

Using the kinetic parameters derived from the last experiment, it is possible to calculate reaction times, monomer addition rates, and

the correct amount of SDAOF catalyst to use so that polymers can be prepared with no detectable monofunctional contaminants. One set of conditions was mentioned earlier which gave 100% difunctional poly-HFPO of $\overline{MW}$ 3200. Polymer with $\overline{MW}$ ~6000 which is cleanly bifunctional can be routinely prepared. Careful control of reaction conditions leads to somewhat higher $\overline{MW}$ polymers with the structure:

$$\underset{\underset{CF_3}{|}}{FOCCF}(OCF_2\underset{\underset{CF_3}{|}}{CF})_n OCF_2 CF_2 O(\underset{\underset{CF_3}{|}}{CFCF_2}O)_m \underset{\underset{CF_3}{|}}{CFCOF} \tag{31}$$

$$n + m = 50$$

The virtual chemical inertness of the backbone structure allows a wide variety of chemical reactions to be done with the quite reactive acyl fluoride end groups.

An example is the preparation of a triazine cross-linked elastomer using the general technique of Ref. 16.

$$R_f(COF)_2 \xrightarrow[NaF]{C_2H_5OH} R_f(COOC_2H_5)_2 \xrightarrow{NH_3} R_f(CONH_2)_2$$

$$R_f(CONH_2)_2 \xrightarrow{P_2O_5}$$

$$\underset{\underset{heat}{\downarrow}}{R_f(\overset{\overset{NH_2}{|}}{C=NH})_2} \xleftarrow{NH_3} \quad R_f(CN)_2 \xrightarrow{catalyst, heat} \tag{32}$$

Triazine elastomers prepared from difunctional poly-HFPO show glass transition temperatures of -50 to -60°C, very good thermal stability at 400°C, and resist hydrolysis.

CONCLUSIONS

Our study of the polymerization of HFPO has led to a better understanding of the mechanism of this living anionic process. Tetraglyme

solutions of cesium alkoxides prepared from perfluorinated acyl fluorides correspond to the propagating species and are more effective initiators than fluoride ions. As the polymerization proceeds, expulsion of cesium fluoride from the alkoxide end groups leads to the creation of new chains and severely limits the molecular weight. Perfluorinated olefin diluents appear to trap some active fluoride ions and lead to higher molecular weight polymers than without such solvents.

Difunctional initiators lead to polymer mixtures containing both monofunctional and difunctional molecules. The kinetic investigation of chain transfer has led to approximate values for the rates of propagation and chain transfer. These data have permitted calculation of conditions for the preparation of cleanly difunctional polymers. These difunctional HFPO polymers undergo a wide variety of chemical reactions at the acyl fluoride endgroups.

Techniques have been developed for the preparation of some chain extended and cross-linked higher molecular weight elastomers that possess outstanding low temperature flexibility, high temperature stability, and chemical inertness [19].

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